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CALCULATION OF MULTICOMPONENT GLASSES BASED ON THE PROPERTIES OF THEIR CONSTITUENT COMPONENTS

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A method is proposed for calculating the composition dependences of various properties of three-component alkali-silicate glasses in the systems $Na_2O – K_2O – SiO_2$ and $Li_2O – K_2O – SiO_2$, one component of which is the homogenizing alkali oxide K_2O. The dependences of the corresponding properties on the alkali oxide content in the two-component alkali-silicates systems $Li_2O – SiO_2$, $Na_2O – SiO_2$, and $K_2O – SiO_2$ were used as parameters in the computational relation. Comparing the computed data and experimental measurements for the density and refraction supports the assumptions forming the basis of the proposed model.

Key words: three-component alkali-silicate glasses, density, refraction, computational method.

In calculations of multicomponent glasses, doubt has always been cast on the possibility of using directly the properties of the components in the free crystalline or glassy state because these properties change under interactions with other components [1]. Instead, the concept of a partial molar property of a component, which depends on its molar content and on the presence of other components in the glass, is used.

It has been shown in [2 – 4] that the concept of partial molar properties can be used in a way so that it will correspond to the properties of the component in a free crystalline or glassy state (in what follows, simply a free state) and does not depend on the properties of two-component glasses. For this, it proposed that the expression describing the composition dependence of a property of the glass be written in a form so that the contribution of each component to the property of glass would be determined as a derivative of this property in the free state and its molar fraction in the glass, while the interaction between the components is taken into account by a separate term:

$$y = y_0 z + y_1 x_1 + y_{01} x_1 z, \qquad (1)$$

where $x_1 + z = 1$; y, y_0, and y_1 characterize the properties of the glass and its constituent components in the free state; y_{01} characterizes the interaction between the components; and, x_1 and z are molar fractions of the components possessing the properties y_1 and y_0.

The composition of the glass is expressed in terms of the content of the oxides, which are treated as components [1]. Since in this approach each component behaves as a structural formation whose properties change because of the interaction with other components, it is proposed that these formations be called structural elements, retaining the term "components" for the corresponding oxide in its free state.

For some glasses there exists a range of compositions where stable combinations of the initial oxides should be regarded as components; specifically, their properties in the "free state" should be reflected in Eq. (1).

A negative interaction indicator y_{01} indicates nonuniformity in the composition range studied. Such glasses are prone to liquation. A method for evaluating this quantity is presented in [3]. In what follows we shall use the concept of a glass-forming agent, i.e., a component which itself can exist in the glassy state or manifest its glass-forming properties in combination with other components, and a modifier, i.e., a component which does not form glass but only changes a property of the glassy structure created by the glass-forming agent.

Positive values of y_{01} correspond to uniform distribution of the structural elements. For a random distribution of structural elements of the glass former and modifier, the nearest-neighbor environment of each element is likewise random.

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For example, an element of a structure-forming agent can be present either in an environment consisting of the same elements or only elements of the modifier correspond to it or both types of elements correspond to it. Here, each relative arrangement of the structural elements corresponds to its own local value of the properties y, which for a glass-forming agent without a modifier addition varies from y_0 to y_0', when only elements of the modifier reflect the structural element of the glass-forming agent. If the averaged property of the structural element of one component (y_{0x} or y_{1x}) is linearly dependent on the content of another component expressed in molar fractions, then we can write for the glass-former and modifier

$$\left.\begin{aligned} y_{0x} &= y_0 + (y_0' - y_0)x; \\ y_{1x} &= y_1 + (y_1' - y_1)z, \end{aligned}\right\} \qquad (2)$$

where y_1 and y_1' are the properties of the structural element of the modifier in the absence of a glass former and when it is surrounded only by elements of the glass former.

A property of glass is determined by averaging it over all elements of the glass-former and modifier. Taking account of their relative content we obtain

$$y = y_{0x} z + y_{1x} x.$$

Using Eq. (2) we obtain Eq. (1), where

$$y_{01} = y_0' - y_0 + y_1' - y_1.$$

Thus, assuming the local properties of each structural element to be linearly dependent on the content of another element expressed in molar fractions, the interaction index remains constant as a function of the glass property. In this case the properties of a two-component glass is a parabolic function of the content of one of the components, where the parameters of the parabola are determined by the partial properties of the structural elements in the free state (properties of the components) and the interaction index (in what follows, the parameters of the function).

In general, in multicomponent systems the magnitude and character of the interaction between all components must be taken into account. If the glass contains one glass former and several modifiers, then its properties can be calculated, to a first approximation, assuming the modifiers to interact only with the glass-former.

Let us consider glass with one glass-former C and two modifiers A and B which do not interact with one another directly:

$$x_1 A - x_2 B - zC,$$

where x_1, x_2, and z are the molar fractions of the modifiers and the glass-former, respectively.

We shall assume the parameters of the function of the property y in each of the two-component glasses ($x_1 A - z_1 C$ and $x_2 B - z_2 C$), containing a glass former C and only one of the modifiers — A or B — to be known:

$$\left.\begin{aligned} y1 &= y_0 z_1 + y_1 x_1 + y_{01} x_1 z_1; \\ y2 &= y_0 z_2 + y_2 x_2 + y_{02} x_2 z_2; \\ z_1 &= 1 - x_1; \qquad z_2 = 1 - x_2, \end{aligned}\right\} \qquad (3)$$

where $y1$, $y2$, y_{01}, and y_{02} are the properties of y and the interaction indices for two-component glasses with the modifiers A and B, respectively.

When two modifiers are present the expression (1) becomes

$$y = y_0 z + y_1 x_1 + y_2 x_2 + (y_{01} x_1 + y_{02} x_2) z, \qquad (4)$$

where $x_1 + x_2 + z = 1$.

It is assumed that the modifiers do not interact with one another directly, since they do not form the corresponding compounds but each one can influence the character of the interaction of the other modifier through it via the glass former.

We know that for certain alkali-silicate glasses the character of the interaction between the components can change depending on the amount of modifier present [2]. In some glasses the modifier and glass-former interact in such a way (in a certain range of the modifier content) that they form structural elements that do not coincide with the initial components. The result is that the structural elements form a separate phase, the modifier distribution in the glass is nonuniform, the glass is prone to liquation, and the structure is loose. Two quasiphases are formed; there is no sharp boundary between them because of the elevated concentration of vacancies in the boundary region, which produces the looseness and the impression that the structure is uniform. The boundary of this range is determined by the composition of the structural element containing the modifier. When a modifier is added, the structure of the glass changes in a way so that in describing the properties the distribution of the glass-former and modifier can be regarded as uniform in this composition range.

For modifiers such as Na_2O and K_2O the former is prone to forming structural elements which correspond to $Na_2O - 4SiO_2$ in some composition range ($0 < x_1 < 0.2$). They comprise a continuous quasi-phase which "envelopes" the silica framework. The parameters of the function $y(x_1)$ — see the expression (1) — in this range are y_{11} and y_{011}. Outside this range ($x_1 > 0.2$) the first modifier dissolves uniformly in the silica, and for glasses with compositions in this range we shall denote the parameters of the function $y(x_1)$ as y_{12} and y_{012}.

The other modifier (K_2O) uniformly dissolves in the silica in the entire range of compositions ($x_2 > 0$) which correspond to the glassy state. Since this modifier is known to have homogenizing effect, its presence as a second modifier changes the parameters of the effect of the first modifier on $y(x_1, x_2)$ in the interval $0 < x_1 < 0.2$. This is expressed in the fact that part of the first modifier dissolves uniformly in the

TABLE 1.

Modifier	Density, g/cm³ / refraction					
	y_{11}	y_{011}	y_{12}	y_{012}	y_2	y_{02}
Li_2O	2.800	– 0.247	1.960	1.03	–	–
Na_2O	3.55	– 0.52	2.54	0.79	–	–
	0.3902	0.0412	0.2910	0.0816		
K_2O	–	–	–	–	2.30	1.07
					0.2920	0.0912

glass former, i.e., its interaction with this part is determined not by the parameters y_{11} and y_{011} but rather by the parameters y_{12} and y_{012}. The parameters of the effect of the remaining fraction of the modifier remain unchanged.

Assuming the contribution of each type of distribution of the first modifier to be proportional to the fraction of each modifier present with respect to the overall content, we can write

$$\left.\begin{aligned} y_1 &= y_{11}\frac{x_1}{x_1+x_2} + y_{12}\frac{x_2}{x_1+x_2};\\ y_{01} &= y_{011}\frac{x_1}{x_1+x_2} + y_{012}\frac{x_2}{x_1+x_2}. \end{aligned}\right\} \qquad (5)$$

Thus, in the expression (4) the parameters y_1 and y_{01} of the effect of the first modifier on the y become dependent on the composition.

The effectiveness of this model was checked for glass in the systems $Na_2O - K_2O - SiO_2$ and $Li_2O - K_2O - SiO_2$, where the first modifiers in a certain composition range (0 – 0.20 for Na_2O and 0 – 0.33 for Li_2O) are prone to separate while the second modifier K_2O, which is common to these glasses, dissolves in the glass former in the entire range of known compositions and possesses the homogenization property. The density $\rho(x_1, x_2)$ and refraction $L(x_1, x_2)$ as functions of the composition were considered as $y(x_1, x_2)$. A parabolic function was fit directly to the experimental data on the density, and a fit was made to the refraction data after the refractive index $n(x_1, x_2)$ data were transformed:

$$L = \frac{n^2 - 1}{n^2 + 2}.$$

The calculations were performed using the relation (4), where the expressions (5) were used instead of y_1 and y_{01}. The parameters of the fitting functions (3) are presented in Table 1.

The corresponding parameters for the glass former SiO_2 are $y_0 = (2.203\ g/cm^3)/0.273$.

The parameters of the fit to the density of two-component glasses as a function of the composition were obtained by analyzing reference data:

for $Li_2O - SiO_2$ — S. K. Dubrovo and Yu. A. Shmidt ($0 < x < 0.5$);

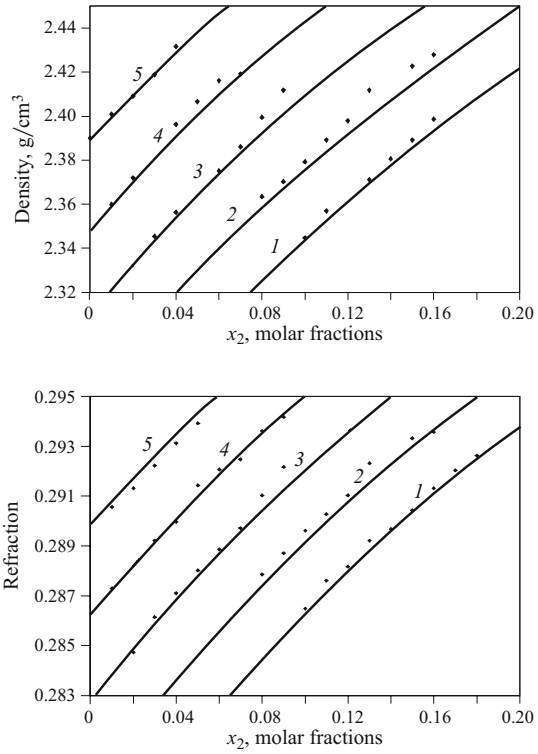

Fig. 1. Density and refraction for glass in the system $Na_2O - K_2O - SiO_2$ versus the K_2O content with different but constant Na_2O content (mol.%): *1*) 0.04, *2*) 0.08, *3*) 0.12, *4*) 0.16, *5*) 0.20 (experimental points — L. N. Urusovskaya [6]).

for $Na_2O - SiO_2$ — Zh. V. Morei and G. E. Mervin ($0 < x < 0.5$);

for $K_2O - SiO$ — Yu. A. Shmidt and Z. D. Alekseeva ($0 < x < 0.33$).

Data for the refractive index dependences were used to determine the fitting parameters for the refraction as a function of the composition of two-component glasses:

for $Na_2O - SiO_2$ — Zh. V. Morei and G. E. Mervin ($0 < x < 0.54$);

for $K_2O - SiO_2$ — Yu. A. Shmidt and Z. D. Alekseeva ($0 < x < 0.33$).

The computed curves for three-component glass were compared with the data obtained by L. N. Urusovskaya [6] and F. K. Aleinikova and coworkers [6]. L. N. Urusovskaya's data, which included the composition dependences of the density and refractive index made it possible to compare the dependence of the $y(x_2)$ when the content of the first modifier (Na_2O) was constant and treated as a parameter. These experimental points as well as the computed curves with $x_1 = 0.04$, 0.08, 0.12, 0.16, and 0.20 molar fractions are presented in Fig. 1. It can be concluded from them that the computed curves not only reflect the character of the dependence quantitatively, but they can also serve as a criterion for determining the possible errors in the individual measurements — these points "fall off" of the smooth curve.

F. K. Aleinikov, I. P. Vaitkus, and I. I. Zhitkyavichute employed another method of obtaining results [6]. They

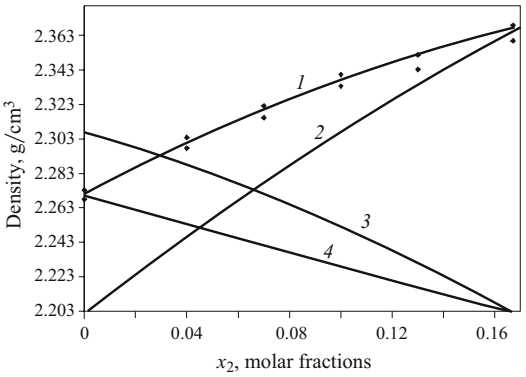

Fig. 2. Density of glass in the system $Li_2O – K_2O – SiO_2$ versus the amount of K_2O with constant content (molar fractions) of SiO_2, $x_1 + x_2 = 0.617$ (experimental points — F. K. Aleinikov, et al. [6]): *1*) computed curve; *2*, *3*) density dependences on the content of each modifier in two-component glass; *2*) $K_2O – SiO_2$ system; *3*) $Li_2O – SiO_2$ system in modifier solving regime; *3*) $Li_2O – SiO_2$ system in delamination regime.

measured the density and other characteristics of the three-component glasses in the system $Li_2O – K_2O – SiO_2$ with different content of modifiers at constant concentration of the glass-former: $x_1 + x_2 = 0.167$. Figure 2 shows a comparison of the data obtained and the results presented in [6]. Since the measurements were performed at temperature 150°C and the computed curve was constructed using parameters determined at 20°C, the authors' data are shown together with points referred to temperature 20°C. Here the method of determining computational parameters that is presented in [3] is used. In terms of the notation used in the present work $y = \alpha\rho$, and the relation (4), where $y_0 = 10^{-6}$ refers to SiO_2, $y_1 = 7.57 \times 10^{-5}$ to $Li_2O – SiO_2$, $y_2 = 1.32 \times 10^{-4}$ to $K_2O – SiO_2$, and $y_{01} = y_{02} = 0$, is used in the calculations. Here

$$\rho_{20} = \rho_{150} + 3y\,(150 – 20),$$

where ρ_t is the density at the temperature t and α is the CLTE.

Comparing the experimental points with the computed curve shows that the contribution of the first modifier corresponds to their separation regime (see Fig. 2, sum of the coordinates of the curves *2* and *4*). The difference of the experimental values from the theoretical values can be explained by the error in choosing the initial parameters. For example, y_0 can vary in the range 2.199 – 2.203 g/cm^3.

Comparing the computed and experimental data one can conclude that the model proposed here describes well glasses with a total content of the modifiers about 0.2 molar fractions.

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